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Nanomaterial transfer using hot embossing for flexible electronic devices

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We demonstrate hot embossing to pattern carbon nanotubes (CNTs) on flexible substrates. Patterns of CNTs grown on both microtextured and flat silicon templates were transferred into polymer substrates, with good replication of both the CNT patterns and surface relief features. The transferred CNTs formed a highly entangled network with electrical resistance of 1 kΩ–9 MΩ, depending on growth and embossing conditions. The electrical properties showed a strong sensitivity to both light and temperature. This dry transfer process shows promise for high throughput manufacturing of nanomaterial-based flexible electronic devices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2178414]

One-dimensional semiconductor nanomaterials are attractive for creating a wide range of macroelectronics and sensors on flexible substrates due to their excellent transport mobilities, along with novel optoelectronic and piezoelectric properties.[1–4] Previous research has shown that random carbon nanotube (CNT) networks may possess electron mobilities as high as 270 $cm^2/V\,s$ and transistor on-off ratios as high as 10^4,[5] while microsilicon networks exhibit transport mobilities near 180 $cm^2/V\,s$.[6] Combining these inherently flexible materials with polymer and paper substrates could yield low-cost high-performance devices which cannot be produced using current semiconductor processing methods. Flexible electronics device manufacture from nanomaterial building blocks is a key challenge, as direct synthesis of nanomaterials on flexible substrates is typically forbidden due to material-processing incompatibilities.

A few methods have attempted to address this challenge of incorporating high-mobility nanomaterials into flexible substrates, either by self assembly or direct printing on polymer substrates.[1,7–13] In general, the processing technologies can be classified as solution-based or dry transfer printing.[7,8,10,11,13] In solution-based printing such as spin casting, flow-directed alignment, or electrophoretic trapping, the nanomaterials are suspended in an "ink" solution which is used to transfer the material to the substrate. These techniques can be used to pattern a wide range of features and are amenable to high throughput manufacturing. However, care must be taken in developing the particle/solution/substrate chemistry to ensure material compatibility. Dry transfer printing techniques use stamps to transfer the nanomaterials to a variety of substrates and may be done without[11–13] or with the assistance of an electric field. Dry transfer printing methods can be advantageous over solution-based processing as they do not require substrate-fluid compatibility.

This letter describes a dry transfer printing method based on hot embossing to integrate conductive nanomaterials into flexible polymer substrates. Nanomaterials are transferred from a microfabricated master template into a thermoplastic substrate during an embossing process. The transfer can be made from a master template that is either smooth or microtextured. The technique is compatible with nanomaterial synthesis techniques that use the vapor-liquid-solid or vapor-solid growth mechanism. The current technique differs from other dry transfer printing methods in that the nanomaterials are synthesized directly on the master template in discrete patterns and transferred to the polymer substrate with no intermediate steps. Surface relief replication of the master occurs during the nanomaterial transfer.

Aligned CNTs were grown on silicon master templates, and then transferred into poly(methylmethacrylate) (PMMA) near the PMMA glass transition temperature, T_g. Patterning of the catalyst and the resulting nanotubes was independent of surface texture. Smooth master templates transferred the CNTs to the polymer without significantly affecting polymer topography, while microtextured master templates transferred both the CNTs and surface relief pattern into the polymer. Figure 1 shows the master template fabrication process.

Master templates were fabricated from standard silicon wafers having a SiO_2 surface layer. Evaporated iron catalyst films (10 nm thickness) were patterned on the SiO_2 using photolithography and a standard lift-off technique. The iron catalyst was patterned in parallel lines 8 mm × 10 μm with line pitch varying 10–500 μm. Microtextured templates were prepared using an additional plasma etch to form textures of height 40 μm. While the catalyst could be patterned

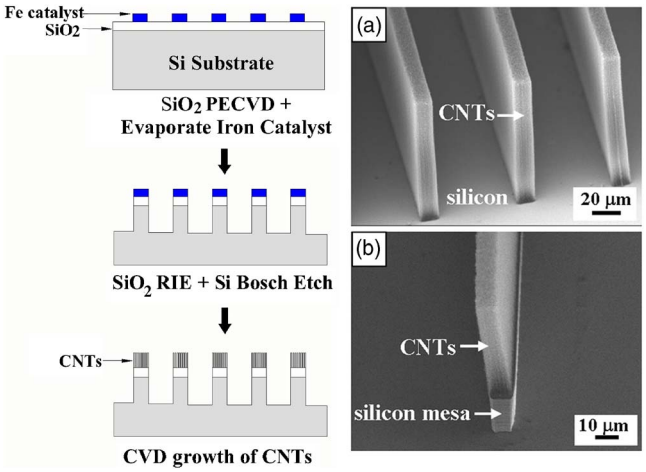

FIG. 1. (Color online) Schematic of master template preparation scheme (left) and the growth of aligned carbon nanotubes on smooth and textured templates (right).

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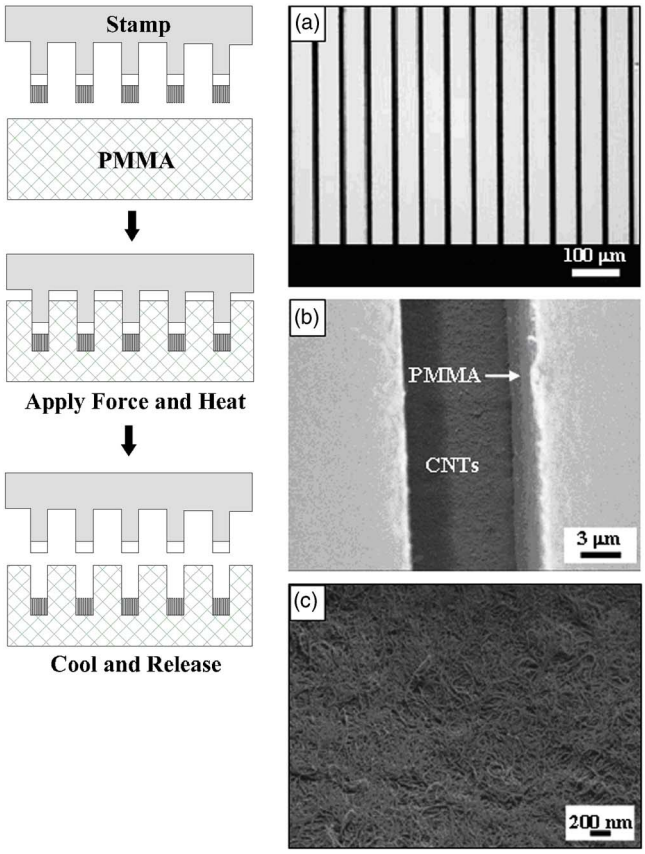

FIG. 2. (Color online) Schematic showing the hot embossing material transfer process (left) and images of the carbon nanotube patterns transferred into PMMA (right). The images show (a) an optical micrograph of CNT transfer from a smooth master template, (b) SEM image of carbon nanotube transfer from microtextured master template, and (c) magnified image of CNT arrangement in polymer trench from image (b).

anywhere on the microtextured template surface, only catalyst patterned on top of the mesas is discussed here.

To synthesize CNTs, the wafer was diced placed into a high temperature chemical vapor deposition furnace. The templates were preheated to the temperature of 660–900 °C in argon, and then exposed to a mixture of acetylene, hydrogen, and methane in a 1:5:10 ratio for growth periods of 3–15 min. After synthesis, the templates were placed in a hot press on a PMMA substrate and heated to 65 °C under load (Fig. 2). After cooling to room temperature, the load was released and the master removed from the substrate.

Carbon nanotube synthesis on the silicon master templates produced well-controlled dense patterns with vertical alignment as shown in Fig. 1. Scanning electron microscopy (SEM) images showed that the nanotubes were of height 5–100 μm, depending upon process conditions. Raman spectra showed the nanotubes were highly graphitic and transmission electron microscopy showed the CNTs were predominately multiwalled.

Figure 2 shows the CNTs in the polymer, showing very good replication. Inspection of the master template revealed that the majority of the carbon nanotubes were transferred into the polymer substrate. The CNTs remaining on the master were sparse and were only visible under SEM. The transfer of the nanotubes into the polymer is can be attributed to two mechanisms: (1) the adhesion of the nanotubes to the deforming polymer when embossed near T_g, and (2) entanglement in the nanotube network which occurs during

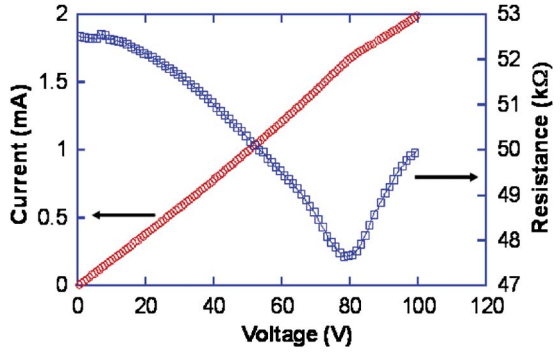

FIG. 3. (Color online) Voltage vs current and voltage vs resistance for a single line CNT trace transferred to PMMA.

aligned growth. The entanglement of CNTs can result in large areas of nanotubes being transferred from interlocking forces. Such an effect is key to manipulating continuous nanotube films pulled from CNT forests.[14] The CNT pattern was transferred in parallel with the surface relief of the template mesa, resulting in the printing of nanotubes at the base of a trench formed in the polymer (Fig. 2). Vertical control is thus possible during nanomaterials printing by embossing with textured templates. Raman spectra showed no structural change in CNTs following transfer.

Electrical characterization of the CNT traces was performed using a standard field effect transistor structure. First, wires were attached to the ends of the nanotube traces to form the source and drain contacts. Parylene (1 μm) was evaporated over the devices to serve as a gate dielectric for an evaporated Au gate electrode. Gate lengths were 6–8 mm. Current-voltage characteristics were measured using a source meter. The tests showed linear *I-V* responses for source-drain voltages up to 30 V. Gate biases to 250 V showed no effect on the *I-V* response; subsequent tests were performed on devices without a top gate contact due to the lack of a transistor-like response. Resistance values ranged between 1 kΩ–9 MΩ across all samples. For a single die, resistance variations of ±20% across ten CNT traces could be obtained. An increase in sample resistance was also observed with bending strain. In addition, impedance measurements between 1 and 30 MHz revealed no frequency dependence, showing some attributes of simple metallic resistors.

Figure 3 shows the typical *I-V* response of a CNT trace without a gate electrode. For this sample, the room temperature resistance was 52.5 kΩ but decreased with increasing applied power due to self-heating above 10 V which was also confirmed using infrared thermography. The CNT network exhibited a linear but negative temperature coefficient of resistance near −51.3 Ω/°C, typical of semiconductors. This behavior is indicative of the thermally induced excitation of charge carriers in the nanotube network. In general, the temperature coefficient of resistance (TCR) was 0.04%–0.1%/°C for all samples. For voltages above 80 V, a permanent residual increase in resistance was observed which was associated with the melting of the PMMA and significant deformation of the CNT traces. Further exploration of the effect of deformation on the nanotube network through bending experiments was also performed. Bending of the samples out to 2.5% strain resulted in an increase of approximately 3% in resistance. After releasing the load, a residual increase of about 1% was observed due to the de-

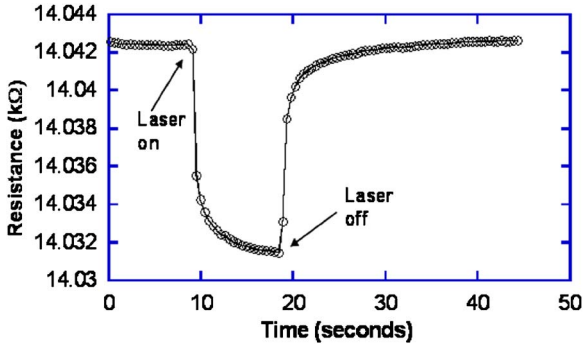

FIG. 4. (Color online) Data showing the change in the resistance of multiwall carbon nanotube traces upon exposure to a 3.8 mW 488 nm Ar+ laser. The data show a decrease in resistance due to the excitation of charge carriers upon the exposure to visible light.

formation showing very minor effects on sample behavior for small strain applications.

While changes in sample resistance with increasing voltage could be explained by heating, an additional drift in the resistance was also observed under ambient lighting, due to the excitation of photoelectrons and charge trapping. To explore this effect, several samples without a gate electrode were exposed to visible light for periods of time under isothermal conditions. Monitoring of the sample resistance with a nominal resistance of 14–30 kΩ revealed that the exposure of the devices to ambient lighting caused the resistance to decrease at the rate of 0.5–1 Ω/min, while placing the samples in a sealed dark chamber caused the resistance to increase at the same rate. This transient rate of change of sample resistance was seen to increase with increasing temperature which is indicative of thermally activated charge trapping. To provide more quantitative measurement of the photoconductive effect, the samples were exposed to a 488 nm Ar+ laser with varying laser power up to 20 mW. The changes in the CNT resistance could be readily observed for laser powers as low as 100 μW. Representative data are shown in Fig. 4, revealing the sensitivity of these simple devices to visible light which behave as semiconductor devices in this application.

This letter reports a method for integrating nanomaterials into flexible polymer substrates by use of hot embossing imprint lithography. The use of dry transfer printing with microtextured stamps allows nanomaterials to be printed into polymer substrates with control over the depth of material printing. Such printing capabilities are of interest for printing new types of macroelectronics, or embedding field emission devices in polymers to make flexible displays. While this work uses carbon nanotubes, the technique is extendable to other nanomaterials that can be synthesized from the vapor liquid solid growth mechanism. Thus, the printing of high mobility semiconductor nanomaterials or oxide semiconductors may yield low-cost macroelectronics in flexible substrates with unique optical, electrical and piezoelectrical properties.

[1]X. Duan, C. Niu, V. Sahi, J. Chen, J. W. Parce, S. Empedocles, and J. L. Goldman, Nature (London) **425**, 274 (2003).
[2]C. K. M. Fung, V. T. S. Wong, R. H. M. Chan, and W. J. Li, IEEE Trans. Nanotechnol. **3**, 395 (2004).
[3]E. S. Snow, J. P. Novak, P. M. Campbell, and D. Park, Appl. Phys. Lett. **82**, 2145 (2003).
[4]P. Yang, Y. Wu, and R. Fan, Int. J. Nanosci. **1**, 1 39 (2002).
[5]Y. Zhou, A. Gaur, S.-H. Hur, C. Kocabas, M. A. Meitl, M. Shim, and J. A. Rogers, Nano Lett. **4**, 2031 (2004).
[6]E. Menard, K. J. Lee, D. Y. Khang, R. G. Nuzzo, and J. A. Rogers, Appl. Phys. Lett. **84**, 5398 (2004).
[7]C. R. Barry, N. Z. Lwin, W. Zheng, and H. O. Jacobs, Appl. Phys. Lett. **83**, 5527 (2003).
[8]G. Blanchet and J. Rogers, J. Imaging Sci. Technol. **47**, 296 (2003).
[9]G. B. Blanchet, S. Subramoney, R. K. Bailey, G. D. Jaycox, and C. Nuckolls, Appl. Phys. Lett. **85**, 828 (2004).
[10]H. O. Jacobs and G. M. Whitesides, Science **291**, 1763 (2001).
[11]M. A. Meitl, Z. Yangxin, A. Gaur, J. Seokwoo, M. L. Usrey, M. S. Strano, and J. A. Rogers, Nano Lett. **4**, 1643 (2004).
[12]Y. Sun, D.-Y. Khang, F. Hua, K. Hurley, R. G. Nuzzo, and J. A. Rogers, Adv. Funct. Mater. **15**, 30 (2005).
[13]Y. Sun and J. A. Rogers, Nano Lett. **4**, 1953 (2004).
[14]M. Zhang, K. R. Atkinson, and R. H. Baughman, Science **306**, 1358 (2004).